Ch 4. Rate constants

Law of mass action

The law of mass action is not really a rate constant. It is more of an equilibrium constant. Suppose we have a general reaction involving gaseous $X$, aqueous (solvated) $A$, liquid $L$, and solvent $S$ reactants $R$ and products $P$. Denote the stoichiometric coefficients by the corresponding lowercase letters. The reaction can be written as

$$
\sum_i x_i^R X_i^R + \sum_j a_j^R A_j^R + \sum_k l_k^R L_k^R + \sum_m s_m^R S_m^R \rightarrow \sum_i x_i^P X_i^P + \sum_j a_j^P A_j^P + \sum_k l_k^P L_k^P + \sum_m s_m^P S_m^P.
$$

This lets us write the Gibbs energy of reaction. Equilibrium occurs when $\Delta G = 0$.

$$
\Delta G = \sum_i x_i^R G_{X_i}^R + \sum_j a_j^R G_{A_j}^R + \sum_k l_k^R G_{L_k}^R + \sum_m s_m^R G_{S_m}^R - \sum_i x_i^P G_{X_i}^P + \sum_j a_j^P G_{A_j}^P + \sum_k l_k^P G_{L_k}^P - \sum_m s_m^P G_{S_m}^P.
$$

Now, we need to know how to write the Gibbs free energy of particular species. Recall that

$$
G = H - TS = U - PV - TS.
$$

Typically, we work at constant temperature. This allows us to compute $S$ for different species. For example,

$$
S_{\text{gas}}(P) = \int_P^P dS = \frac{1}{T} \int_P^P dQ = -\frac{1}{T} \int_P^P \frac{NkT}{P} dP,
$$
so we find that
\[ S_{\text{gas}}(P) = -k \ln P \text{ per atom or molecule.} \]

The lower the pressure, the higher the volume, so the more space the molecule can visit and hence the higher the entropy. Similarly,
\[ S_{\text{solute}}(C) = -k \ln C \text{ per atom or molecule,} \]
where \( C \) is the solute concentration. Basically, the less solute there is, the more entropy each solute molecule has (just like the gas), although if you add more solute molecules, there is more overall entropy (summed over all the molecules). There are no similar effects for liquids or solvents, because they basically always take up the same volume and hence do not experience large changes in configurational entropy.

The standard Gibbs free energy \( G^\circ \) is computed at the standard conditions \( p^\circ = 1 \text{ atm}, C^\circ = \frac{1 \text{ mol solute}}{\text{kg solvent}} \), which returns \( H^\circ \) and \( S^\circ \). Therefore, \( G(P) = G^\circ + kT \ln(\frac{P}{P^\circ}) \).

Inserting the forms of the Gibbs free energy (and the standard Gibbs free energy) into our above expression and setting the overall \( \Delta G = 0 \), for equilibrium, gives us the relation
\[
\frac{-\Delta G^\circ}{kT} = \sum_i x_i^p \ln(\frac{P_{X_i}^p}{P^\circ}) - \sum_i x_i^R \ln(\frac{P_{X_i}^R}{P^\circ}) + \sum_j a_j^p \ln(\frac{C_{A_j}^p}{C^\circ}) - \sum_j a_j^R \ln(\frac{C_{A_j}^R}{C^\circ}).
\]

This holds as long as there are both solids and liquids still in the reaction. If you ran out of solid, for example, the reaction would not reach equilibrium - it would stop before reaching equilibrium. Exponentiating both sides of the equation gives the equilibrium constant
\[
K_{\text{eq}} = e^{-\frac{\Delta G^\circ}{kT}}.
\]

The point of the equilibrium constant is that it is defined for standard conditions; we measure everything relative to standard conditions. So at equilibrium, the pressures and concentrations of the gaseous and aqueous phases must satisfy
\[
K_{\text{eq}} = \frac{\prod_i (\frac{P_{X_i}^p}{P^\circ})^{x_i^p} \prod_j (\frac{C_{A_j}^p}{C^\circ})^{a_j^p}}{\prod_i (\frac{P_{X_i}^R}{P^\circ})^{x_i^R} \prod_j (\frac{C_{A_j}^R}{C^\circ})^{a_j^R}}.
\]

If you want to make the same product and have extra gas, then you need less solute.

**About rate constants**

Catalysis is concerned with speeding up reactions. So, we need dynamics, not just equilibrium properties: we need to know how to speed up reactions.

There is a timescale problem in simulating rare events, which is why computer simulations of reactions are often not very good. The important elementary reactions are the slowest, or rate-determining, ones. Because these reactions are slow, the probability of collision in these reactions is small. Hence, the computational power involved in simulating them is often overbearingly long.
Also, this magnifies any mistakes or shortcomings in the model of the potential energy surface provided by the theoretician.

We will, instead, look at transition rate theory (TST), which provides simple estimates of the rate based on the potential energy surface. We will treat it classically and replace some parts with quantum mechanics when necessary. Often, the quantum effects are pretty small, at high-enough $T$.

Our main result in this chapter will be that the rate constant $K$ for an elementary reaction is given by

$$K = \frac{kT}{\hbar} e^{-\Delta G_{TS}^\circ/kT}.$$  

Here, $\Delta G_{TS}^\circ = \Delta E_{TS}^\circ - T\Delta S_{TS}^\circ$ is the standard Gibbs free energy in the transition state, minus the standard Gibbs free energy in the reactant state.

**Transition state theory**

A potential energy surface (PES) describes the energy of a system, typically a collection of atoms or molecules, in terms of certain parameters, normally the positions of the atoms. It is a unique correspondence between a potential energy and the nuclear positions of the system, in the Born-Oppenheimer approximation. The parameters could also include angles and stuff like that. It is the generalization of the Morse potential to more than one parameter. In other words, it generalizes $E(r)$ to $E(\vec{r})$,

where $\vec{r}$ represents the atomic positions, or inter-atomic distances and angles. For a system of $N$ atoms, the dimension of the parameter space is at most $3N$, because that is the dimension of position space. If the atoms are linked (i.e. bonded) in some way, the dimension is lower. We don’t count the momenta in $\vec{r}(t)$ because they don’t contribute to the potential energy, only the kinetic energy. (You can read the article on Wikipedia for more info.)

The transition state splits the parameter space into two regions: the reactant region (R) and the product region (P). The lowest-energy configurations in the reactant region and product region are called the initial state and final state, respectively. The lowest-energy point in the transition state is sometimes also called the transition state; it is often used to make a harmonic approximation or something. If the parameter space is of dimension $d$, the transition state is a $d - 1$-manifold embedded in this $d$-dimensional space.
We shall typically work in the Born-Oppenheimer approximation. This means that the ions move much slower than the electrons. This approximation, common throughout quantum chemistry, assumes that the electrons instantaneously relax to the ground state according to the ionic positions, so that the electrons are never in an excited state; they are always in the ground state, whatever the ground state happens to be for the configuration $\vec{r}(t)$. We also ignore quantum tunneling, focusing on classical effects (okay at high-$T$) and that there are no recrossings. In other words, once the system reaches the transition state with velocity pointing towards the product region, it will necessarily react, and not go back to the reactant region.

Now that we have the assumptions out of the way, let’s study transition state theory. We postulate that the rate constant for an elementary process can be written as

$$K = P_{TS} r_C,$$

where $P_{TS}$ is the probability of being in the transition state and $r_C$ is the rate of passing through the transition state towards the product region. To make $r_C$ finite and to make $P_{TS}$ nonzero, we must assume that the transition state has some finite thickness $\delta x$. This will make more sense in just a second. It will turn out that the $r_C$ part can be derived classically but the $P_{TS,\delta x}$ part cannot, and we will have to go to quantum statistical mechanics for that. I think this is because the velocities can be high at high-$T$, so the kinetic part can be treated classically, but the potential part cannot be treated classically because we are localizing in a very small region, so quantum effects become nontrivial.

Classically, the energy as a function of positions $\vec{x}$ and velocities $\vec{v}$ is

$$E(\vec{x}, \vec{v}) = V(\vec{x}) + \sum_i \frac{1}{2} m_i v_i^2.$$

The probability of visiting a certain point in phase space, using Boltzmann factors, is

$$P(\vec{v}, \vec{v}) \propto P_x(\vec{x}) P_v(\vec{v}),$$

where $P_x(\vec{x}) \propto e^{-V(\vec{x})/kT}$ and $P_v(\vec{v}) \propto e^{-\frac{1}{2} \sum_i m_i v_i^2}$.

We define the rate of traversal across the region of thickness $\delta x$ to be

$$r_c = \frac{|v_\perp|}{\delta x}.$$
You can calculate the average \( v_\perp \) from the Boltzmann distribution. The result is

\[
|v_\perp| = \sqrt{\frac{kT}{2\pi\mu}},
\]

where \( \mu \) is an effective mass (which represents the entire system).

As we said before, we have to get \( P_{TS,\delta x} \) quantum-mechanically. Loosely, this is

\[
P_{TS,\delta x} = \frac{\sum_j e^{-\epsilon_j/kT}}{\sum_k e^{-\epsilon_k/kT}} \approx \frac{Z^{TS}}{Z^R}.
\]

Here, \( Z^{TS} \) is the partition function for being in the \( d-1 \)-dimensional transition-state manifold, \( Z^R \) is the partition function for the entire reactant region, and \( Z^{\delta x} \) is the partition function for being in the 1-dimensional artificial thickness \( \delta x \). We can approximate \( Z^{\delta x} \) if we assume that \( \epsilon_j \) doesn’t change much (i.e. \( \delta x \) is smaller than the characteristic size of energy fluctuations) by the particle-in-a-box energies:

\[
\epsilon_n \approx \frac{(nh)^2}{8\mu\delta x^2} \Rightarrow Z^{\delta x} \approx \int_0^\infty e^{\frac{(nh)^2}{8kT\mu\delta x^2}} dn = \sqrt{\frac{2\pi\mu kT}{h^2}} \delta x.
\]

This is linear in \( \delta x \). Great! It will cancel the \( \delta x \) on the bottom of \( r_C \). The result is

\[
K = \frac{kT Z^{TS}}{h Z^R}.
\]

If we write \( Z = e^{-G^o/kT} \) and \( \delta G_{TS}^o = G_{TS}^o - G_R^o \), this becomes

\[
K = \frac{kT}{h} e^{-\Delta G_{TS}^o/kT}.
\]

**Harmonic TST**

Harmonic transition state theory invokes a harmonic (i.e. second-order) expansion of the potential energy surface both in the initial state and the saddle point separating the initial state and the final state.
It’s pretty nontrivial to determine the transition state point on the transition surface. If you can do so, and if you can determine the harmonic approximations to the energies at the saddle-point on the transition surface and to the initial state

\[ V_R(q_{IS}) = V_{IS} + \frac{1}{2} \sum_{i} k_{IS}^i q_{IS}^i, \]

\[ V_{TS}(q_{SP}) = V_{SP} + \frac{1}{2} \sum_{j} k_{SP}^j q_{SP}^j. \]

The partition function of a single harmonic oscillator with frequency \( \omega \) is

\[ Z(\omega) = e^{-\beta \hbar \omega/2} (1 - e^{-\beta \hbar \omega})^{-1}, \]

because there is a nonzero zero-point energy.

Of course, there are multiple harmonic oscillators - one for each dimension. This approximation lets us find the partition functions in the constant \( K \) for transition rate theory. Just substitute

\[ Z^{TS} = \prod_i e^{-\beta \hbar \omega_{TS}^i/2} (1 - e^{-\beta \hbar \omega_{TS}^i})^{-1}, \]

\[ Z^R = \prod_i e^{-\beta \hbar \omega_{R}^i/2} (1 - e^{-\beta \hbar \omega_{R}^i})^{-1}. \]

If we approximate \( 1 - e^{-x} \approx x \), we get

\[ K_{\text{harmonic}} = \nu e^{-\beta \Delta E_a}, \]

where \( \Delta E_a = (V_{SP} - \sum_{j} \hbar \omega_{SP}^j/2) - (V_{IS} - \sum_{j} \hbar \omega_{IS}^j/2) \), and \( \nu = \frac{\prod_{j} \omega_{IS}^j}{\prod_{j} \omega_{SP}^j} \).

**Ch 5. Kinetics**

“Microkinetic modeling” combines rate constants of multiple elementary steps to arrive at an overall rate. Let’s first study a single elementary step.
Microkinetics: elementary reaction

Suppose we know the rate constants $k_+$ for adsorption and $k_-$ for desorption of species $A$ from a surface. Let $\theta_A$ be the fractional coverage of the adsorbate $A$ and let $\theta_* = 1 - \theta_A$ be the probability that a site is unoccupied. Let * represent the surface; the reaction is

$$A + \ast \iff A^*.$$

We can derive another relationship between $\theta_A$ and $\theta_*$ in equilibrium.

$$0 = \Delta G = G_{\text{ads}} - G_{\text{gas}} = \Delta G^\circ - T(S_{\text{ads}} + k \ln \frac{p_A}{p^o}),$$

where $S_{\text{ads}} = -k \ln \frac{\theta_A}{\theta_*}$ is the configurational entropy. Then

$$\frac{\theta_A}{\theta_*} = K_A \frac{p_A}{p^o} \implies \theta_A = K_A p_A \theta_*,$$

where $K_A = K_{\text{ads}} = e^{-\beta \Delta G^\circ}$ and $p_A$ is now defined as the dimensionless ratio between $p_A$ and $p^o$. So at equilibrium,

$$r_{\text{des}} = r_{\text{ads}} \implies k_- \theta_A = k_+ p_A \theta_* \implies K_{\text{ads}} = \frac{k_+}{k_-}.$$

It’s generally true that equilibrium constants are the forward rate constant divided by the backward rate constant. We can define the reversibility $\gamma$ by

$$\gamma := \frac{\theta_A}{p_A \theta_*} K_{\text{ads}}^{-1},$$

and $\gamma > 1$ means there is too much adsorbed $A^*$, so the reaction tends to go backwards; $\gamma < 1$ means the reaction tends to go forwards. The system is in equilibrium for $\gamma = 1$.

We can generalize this to different elementary steps. For example,

$$A_2 + 2 \ast \iff 2 A^*$$

gives the rates

$$r_{\text{ads}} = k_+ p_{A_2} \theta_*^2, r_{\text{des}} = k_- \theta_A^2.$$

However, the relation $\theta_A = K_A p_A \theta_*$ still holds.

Microkinetics: coupled elementary processes

Okay, let’s combine multiple elementary steps and try to determine the overall rate of reaction for the full catalytic cycle. Consider the simple example $A_2 + B \iff 2 AB$, where the elementary steps are

$$A_2 + 2 \ast \iff 2 A^* \text{ and } A^* + B \iff \text{AB} + \ast.$$

The surface, *, is the catalyst for this reaction. The rates for the two elementary steps are

$$R_1 = k_1 p_{A_2} \theta_*^2 - k_- \theta_A^2, R_2 = k_2 p_B \theta_A - k_- p_{AB} \theta_*.$$
The dynamics of the reaction can be written
\[
\partial_t \theta_A = 2R_1 - R_2.
\]

There are only \( \theta_A, \theta_* \) possibilities in this reaction, so only one differential equation is necessary. Solving this equation for industrial applications is nontrivial because we may need to model different rates at different places in the reactor, spatially-dependent pressures and temperatures, etc.

The overall equilibrium constant and reversibility are
\[
K_{eq} = \prod_i K_i^{n_i}, \gamma = \prod_i \gamma_i^{n_i}.
\]

Here, \( n_i \) is the number of times step \( i \) must be carried out in the overall reaction. For this example, \( n_1 = 1 \) and \( n_2 = 2 \).

There are some approximations that often are used.

- **Steady-state approximation**: \( \partial_t \theta_A = 0 \). This means that the coverage doesn’t change; it does not mean that the overall reaction rate is zero.

- **Strongly rate-determining approximation**: Define reversibilities \( \gamma_i \) for each elementary step \( i \). If there is a “slow step” or “rate-determining step,” the strongly rate-determining approximation sets
  \[
  \gamma_i = 1 \text{ for all } i \neq \text{ slow step},
  \]
  \[
  \gamma_{\text{slow step}} \neq 1 \text{ unless in equilibrium}.
  \]

  This means all elementary steps, except for the slow step, equilibrate quickly.

**Example: ammonia synthesis**

Ammonia synthesis is an industrially relevant process and is a good example of the above analysis. Here are the elementary reactions; the first step is the slow step.

1. \( N_2 + 2* \rightarrow 2N* \)
2. \( H_2 + 2* \rightarrow 2H* \)
3. \( N* + H* \rightarrow NH* + * \)
4. \( NH* + H* \rightarrow NH_2* + * \)
5. \( NH_2* + H* \rightarrow NH_3* + * \)
6. \( NH_3* \rightarrow NH_3 + * \)
Under both steady-state and slow-step approximations, the results for equilibrium surface coverage and reaction rate are

\[
\theta_* = [1 + \sqrt{K_2 p_{H_2}} + \frac{p_{NH_3}}{K_2 p_{H_2} K_5 K_6} + \frac{p_{NH_3}}{K_2 p_{H_2} K_4 K_5 K_6} + \frac{p_{NH_3}}{(K_2 p_{H_2})^{3/2} K_3 K_4 K_5 K_6} + \frac{p_{NH_3}}{K_6}]^{-1},
\]

\[
R = R_1 = k_1 p_{N_2} \theta_*^2 (1 - \gamma), \text{ where}
\]

\[
\gamma = \frac{p_{NH_3}^2}{K_{eq} p_{H_2} p_{N_2}} \text{ and } K_{eq} = K_1 K_2^3 K_3^2 K_4^2 K_5^2 K_6.
\]

### Ch 6. Energy trends in catalysis

Scaling relations are simple approximations that drastically reduce the dimension of “parameter space.” This can give a (quite good) qualitative description of trends in reaction energetics.

#### Chemisorption energy scaling

Generally, it has been found that adsorption energies of different surface intermediates which bind to the surface through the same atoms(s) scale linearly with each other, when the atomic number of the substrate is varied.

For example, consider the adsorption energy of CH$_n$ versus the adsorption energy of atomic carbon, C. To a good approximation,

\[
\Delta E_{CH_n} = \gamma_s(n) \Delta E_C + \xi(n).
\]

Also important is that $\gamma_s(n)$ is independent of how the surface is cut - the cut of the surface affects $\xi(n)$ only.

![Graph showing energy trends for CH$_n$](image)

In fact, we find

\[
\gamma_s(n) = \frac{4-n}{4} \text{ for } CH_n, \quad \gamma_s(n) = \frac{3-n}{3} \text{ for } NH_n, \quad \gamma_s(n) = \frac{2-n}{2} \text{ for } OH_n.
\]

How to understand these slope rules? Suppose we are talking about the atomic species A, which forms $N$ covalent bonds. (Here, A could be C, N, or O.) If we assume these $N$ covalent bonds are
degenerate, separable, and linearly independent, then each contributes the same amount to the total binding energy when \( A \) couples to a surface. Each hydrogen takes away one of these bonds. So,

\[
\text{AH}_n \text{ can make } N - n \text{ bonds, and } A \text{ can make } N \text{ bonds.}
\]

That is why the slope is \( \frac{N-n}{N} \). It is independent of how the surface is cut. Typically, you know the adsorption energies of the base elements \( A \) (C, O, N, S, etc.) and you use the scaling relationship to get the adsorption energies for \( \text{AH}_n \) or something.

**Ch 8. The electronic factor in heterogeneous catalysis**

This chapter studies the orbital theory of chemisorption (adsorption via chemical bonding) of an adsorbate on a transition metal surface.

**d-band model of chemisorption on transition metals**

We would like to understand how chemical reactivity of adsorbates on transition-metal substrates varies with the metal, i.e. with atomic number. To do so, let’s create a mental picture.

Imagine an oxygen atom \( O = [\text{He}]2s^22p^4 \) which approaches a transition-metal surface. Its electrons begin to interact with the electronic states of the surface. For oxygen, the freest electrons are in the \( p \)-orbital.

For the valence electrons of a transition metal, the \( s \) and \( p \)-orbitals are spatially bigger than the \( d \)-orbital. We heuristically group the \( sp \) orbitals together; because they overlap with each other a lot, they form broad, overlapping energy bands. Because the \( d \) orbitals do not overlap very much, they form narrower bands close to the highest occupied state - the Fermi level \( E_F \). Of course, some of the energy band for both \( sp \) and \( d \)-type orbitals must lie beneath the Fermi level; otherwise, they would not be occupied. Typically, at least some of the \( sp \) band is well below the Fermi level. However, it is often the case that all of the \( d \) band is not too far below the Fermi level.

\[
\begin{array}{c}
E \\
\downarrow \\
E_F \\
\uparrow \\
d\text{-band} \\
\hline
sp\text{-band}
\end{array}
\]

Let the oxygen atom approach the surface. We separate the bonding mechanism into two steps.

1. Bonding states are formed between the metal \( sp \)-states and the oxygen \( 2p \) states near the bottom of the \( sp \) bands. Basically, electrons from the \( sp \) metal band “drop into” the unfilled \( 2p \) states of Oxygen; the hybridized energy is lower than either of the energies of the \( 2p \)
states or the \( sp \) states, just like the hybridization of \( H \) with \( H \) to make \( H_2 \). These states are well below the Fermi level, so they are automatically occupied. We say the \( p \)-orbital of oxygen has been totally filled to form adsorbed \( O^{2-} \):

\[
O = [He]2s^22p^4 \rightarrow O^{2-} = [He]2s^22p^6.
\]

We say the oxygen \( 2p \) orbital has been \textit{renormalized}. This is energetically favorable.

![Diagram of atomic energy levels with renormalization](image)

Figure 2: Oxygen atom interacts with \( sp \) transition metal orbitals, “renormalizing” the oxygen \( 2p \) orbital.

2. Now we consider the coupling between the renormalized oxygen \( 2p \) orbital and the metal \( d \) orbital. Because the surface \( d \)-states are narrow, the approach of the renormalized oxygen to the metal surface creates hybrid orbitals: a bonding orbital of low energy and an antibonding orbital of higher energy.

The \textit{strength of the bonding is determined by the occupation of the antibonding states}: The bonding states will always be filled; the bond is stronger if the antibonding states are \textit{not} filled.

In a regular molecule, you can determine whether the antibonding states will be filled simply by counting the number of electrons participating in the bonding process. In this kind of interaction, however, there are an infinite number of electrons which can drop into the antibonding states, so the filling is given by the \textit{position of the antibonding state relative to the Fermi level}. If more of the antibonding “band” is below \( E_F \), the antibonding orbital will be more filled and the bond will be weaker.
In the \(d\)-band model of adsorption, we write the adsorption energy as

\[ \Delta E = \Delta E_{sp} + \Delta E_d, \]

where \(\Delta E_{sp}\) is the contribution from \(sp\)-orbital metal electrons and \(\Delta E_d\) is the contribution from \(d\)-orbital metal electrons. Typically, \(\Delta E_{sp}\) is large and negative, and much greater in magnitude than \(\Delta E_d\).

We assume \(\Delta E_{sp}\) is roughly constant with atomic number (independent of which transition metal we are talking about), which is a reasonable approximation because the number of \(sp\) electrons in the core is constant for transition metals in the same row of the periodic table. Hence, the periodic variation (periodic as in periodic table) of \(\Delta E\) is primarily a \(d\)-band effect.

### Periodic trends of adsorption energy: \(d\)-band center

Oxygen bonds most strongly to transition metals in the upper left of the periodic table. So there are two trends here: decreasing bond strength as we add \(d\)-band electrons in a fixed row of the periodic table, and decreasing bond strength as we go down the periodic table. How can we understand this?

For simplicity, let the variation of bond strength depend only on the position of the \(d\) band center, \(\epsilon_d\). If \(\epsilon_d\) increases, we expect the position of the antibonding orbital, \(\epsilon_{anti}\), to increase as well, and for the antibonding orbital to be less filled and hence for the bonding to be stronger. (In fact, the relevant quantity is the upper edge of the \(d\)-band. \(\epsilon_d\), the center of the \(d\)-band, happens to track well with the upper edge.)

So, why does the \(d\) band center, \(\epsilon_d\), move up as we move left in the periodic table?

Now, we explain the variations in adsorption energy as we move up or down the periodic table. Decompose the \(d\)-band interaction energy into a Pauli repulsion term, \(\Delta E_d^{ortho}\) arising from the orthogonalization of the adsorbate states to the metal states, and a combined bonding-antibonding term \(\Delta E_d^{hyb}\):

\[ \Delta E_d = \Delta E_d^{ortho} + \Delta E_d^{hyb}. \]
Apparently, we can assume that the overlap matrix element scales with the coupling matrix element $V_{a-d}$ (coupling between adsorbate “a” and $d$-band electrons “d”), so

$$\Delta E_{d}^{\text{ortho}} \propto |V_{a-d}|^2.$$ 

**Other trends**

Different surfaces of a given material can produce different $d$-band centers and hence yield different reactivities. For a given metal, *the higher the coordination number, the broader the band*. This is because surfaces with high coordination number have the metal atoms closer together, yielding stronger dispersion.

When the coordination of a surface metal atom is lowered (such as for a step or edge atom), then the width of the $d$-band decreases, forcing the center of the $d$-band upwards. Because the center of the $d$-band is now higher, the surface atoms with lower coordination are more reactive.

![Figure 4: (a) surface metal atom with high coordination (b) lower coordination](image)

Straining the surface (i.e. increasing the lattice constant) decreases the dispersion of the $d$-band and changes $\epsilon_d$ for similar reasons.

**Ch 12. Relation of activity to surface electronic structure**

In this chapter, we study the mathematical theory of hybridization, which is what you get when you put two degenerate fermion levels next to each other. By Pauli exclusion principle, no two fermions can occupy the same quantum state. The result is *hybridization*, or the formation of new orbitals.

Actually, the electrons in the atoms need not be degenerate. The mere overlap of orbitals leads to hybridization, as we will see below.

**Two-atom hybridization**

Let $A$ and $B$ be two atoms. When they are far apart, let the initial states of the electrons be $|\psi_A\rangle$ with eigenenergy $\epsilon_A$ and $|\psi_B\rangle$ with eigenenergy $\epsilon_B$. In the LCAO approximation, we pretend that
the state when the atoms approach each other is a linear combination of the original states,
\[ |\psi_{AB}\rangle = c_1|\psi_A\rangle + c_2|\psi_B\rangle. \]

Defining the overlap matrix elements \( S_{ij} \) and the coupling matrix elements \( V_{ij} \) by
\[
S_{ij} := \langle \psi_i | \psi_j \rangle = \begin{cases} 1 & \text{if } i = j, \\ S & \text{if } i \neq j, \end{cases},
\]
\[
V_{ij} := \langle \psi_i | H | \psi_j \rangle = V.
\]

These matrix elements let us solve for the eigenenergies in the Schrodinger equation
\[ H|\psi_{AB}\rangle = \epsilon |\psi_{AB}\rangle. \]

The result is
\[
\epsilon_{\pm} = \frac{(\epsilon_A + \epsilon_B) - 2SV \mp \sqrt{(\epsilon_A - \epsilon_B)^2 - 4(\epsilon_A + \epsilon_B)SV + 4V^2 + 4\epsilon_A\epsilon_BS^2}}{2(1 - S^2)}.
\]

Often, we assume the dominant terms in the square root are the ones with no \( S \). In the case that \( \epsilon_A = \epsilon_B \) (the original atoms had degenerate energy levels), we find
\[
\epsilon_{\pm} = \epsilon_A + |SV| \mp |V|.
\]

Here, \( S > 0, V < 0 \implies -SV > 0. \) \(-SV\) is the Pauli repulsion term and shifts all energy levels up. The lower energy state is called the bonding state and the higher energy state is called the antibonding state.

This model explains why \( H + H \rightarrow H_2 \) occurs but \( \text{He} + \text{He} \rightarrow \text{He}_2 \) does not. Consider the following picture of the hybridized orbitals,

![Image of hybridized orbitals](image)

The average energy of the hybridized electrons is lower in the hydrogenic reaction but higher in the helium reaction. Hence, \( H_2 \) is observed but not \( \text{He}_2 \). To estimate the length of the hydrogenic covalent bond, approximate \( S = -\gamma V \). Then the energy shift \( \Delta E \) from the original orbital to the bonding orbital is approximately
\[
\Delta E \approx -2|V| + 2\gamma V^2,
\]
which gives an estimate on some optimal \( |V| \), and hence an optimal overlap and an optimal internuclear distance.
Claim: When the energy levels get further and further apart (i.e. when $|\epsilon_A - \epsilon_B|$ increases), the splitting of energy levels due to the interaction decreases.

Reasoning: This follows by approximating (for $\epsilon_A - \epsilon_B \gg V$)

$$\epsilon_{\pm} = \frac{\epsilon_A + \epsilon_B}{2} - SV \mp \frac{\epsilon_A - \epsilon_B}{2} \sqrt{1 + \left(\frac{2V}{\epsilon_A - \epsilon_B}\right)^2}$$

$$\Rightarrow \epsilon_+ \approx \epsilon_A - \frac{V^2}{\epsilon_B - \epsilon_A} - SV, \epsilon_- \approx \epsilon_B + \frac{V^2}{\epsilon_B - \epsilon_A} - SV.$$ 

That was the mathematics. Physically, why does the splitting decrease as the energy levels get further apart?

I am not sure this explanation is right, but here goes: the energy of an electron is related to the “effective volume” it is enclosed in. For example, the energy $E$ of a particle in a box of length $L$ scales as $E \propto \frac{1}{L^2}$. The formation of a covalent bond can be explained as “when you put boxes of lengths $L_A$ and $L_B$ together, you get a box of length $L > L_{A,B}$ which guarantees a lower energy.” If the energies are very different, then $L_A$ and $L_B$ are very different, so the effect of putting these boxes together is not as powerful. But then, it would seem to be powerful for the electron at higher energy, so that doesn’t make too much sense...

Anderson-Newns model

Consider a metal surface with one-electron states $|k\rangle$ with energies $\epsilon_k$ and an adsorbate with a single valence state $|a\rangle$ of energy $\epsilon_a$. Assume $\langle a|k\rangle \approx 0$. Our question is: what is (a good approximation for) the adsorption energy?

Define the matrix elements $H_{ak} = V_{ak} = \langle a|H|k\rangle$, $H_{aa} = \epsilon_a$, $H_{kk} = \epsilon_k$. Use LCAO and expand the solution $|\phi\rangle$ as

$$|\phi_i\rangle = c_{ai}|a\rangle + \sum_k c_{ki}|k\rangle,$$

with corresponding Schrodinger equation

$$H_{ij}c_j = \epsilon_ic_i.$$

The projection of the density of states on the adsorbate state is

$$n(\epsilon) = \sum_i |\langle \phi_i|a\rangle|^2 \delta(\epsilon - \epsilon_i).$$

Physically, this captures the evolution of the adsorbate state. It splits $|a\rangle$ into different solutions of the combined system, $|\phi_i\rangle$, and it is these combined-system solutions which are physically meaningful (and are assigned energies). In other words, for a given $|a\rangle$, it tells us what energies are in the system, and with what strength.

Using the Cauchy principal value, we can write

$$n(\epsilon) = \sum_i |\langle \phi_i|a\rangle|^2 \delta(\epsilon - \epsilon_i) = -\frac{1}{\pi} \langle a|G(\epsilon)|a\rangle,$$
\[ G(\epsilon) = \lim_{\delta \to 0^+} \sum_i \frac{|\phi_i\rangle \langle \phi_i|}{\epsilon - \epsilon_i + i\delta}. \]

We need to solve for \( \langle a | G(\epsilon) | a \rangle = G_{aa} \). We do so by appealing to the matrix equation

\[
(\epsilon - \mathcal{H} + i\delta)G(\epsilon) = 1.
\]

Well, in index notation, it would be

\[
((\epsilon + i\delta)\delta_{ij} - \mathcal{H}_{ij})G_{jk}(\epsilon) = \delta_{ik}.
\]

We want to solve for \( G_{aa} \), so we only need to consider equations with that expression.

\[
G_{aa}(\epsilon + i\delta - \epsilon_a) - \sum_k V_{ak}G_{ka} = 1,
\]

\[-V_{1a}G_{aa} + (\epsilon + i\delta - \epsilon_{11})G_{1a} - \sum_{k=2}^n V_{1k}G_{ka} = 0,
\]

and so on. The solution turns out to be

\[
G_{aa}(\epsilon) = \frac{1}{\epsilon - \epsilon_a - q(\epsilon)}|_{\delta \to 0^+},
\]

where \( q(\epsilon) = \sum_k \frac{V_{ak}^2}{\epsilon - \epsilon_k + i\delta} = \Lambda(\epsilon) - i\Delta(\epsilon) \), and

\[
\Delta(\epsilon) = \pi \sum_k V_{ak}^2 \delta(\epsilon - \epsilon_k) \text{ and } \Lambda(\epsilon) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Delta(\epsilon')}{\epsilon - \epsilon'} d\epsilon',
\]

which is just the Kramers-Kroning relation. Because we took the principal value instead of assigning a contour, it should hold regardless of whether the poles are in UHP or LHP.

The result for the density of states is

\[
n(\epsilon) = -\frac{1}{\pi} \text{Im} G_{aa}(\epsilon) = \frac{1}{\pi} \frac{\Delta(\epsilon)}{(\epsilon - \epsilon_a - \Lambda(\epsilon))^2 + \Delta(\epsilon)^2}.
\]

**Binding energies:** We can estimate the binding energy of the adsorbate to the surface using the Anderson-Newns model. The unperturbed metal system has energy given by

\[
E_{\text{metal + atom}} = \int_{-\infty}^{E_F} \epsilon \rho(\epsilon) d\epsilon + n_a \epsilon_a,
\]

where \( \rho(\epsilon) \) is the density of states (on the surface).

The adsorption of a molecule will change the density of states from \( \rho(\epsilon) \) to \( \tilde{\rho}(\epsilon) \). If we define \( \delta \rho = \tilde{\rho} - \rho \), the binding energy is just

\[
E_{\text{bind}} = \int_{-\infty}^{E_F} \epsilon \delta \rho(\epsilon) d\epsilon - \delta N E_F + n_a E_F.
\]

In the above equation, \( n_a \) is the number of adsorbate atoms which stick to the surface and \( \delta N \) is a change of number of states in the metal (we have to remove some states from the metal to fit the adsorbate energy levels in). The binding energy as defined above must be negative for the adsorption to be thermodynamically favorable.